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# Synthesis and Characterization of Phosphorescent Two-Coordinate Copper(I) Complexes Bearing Diamidocarbene Ligands

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## Abstract

The photophysical properties of four, two-coordinate, linear diamidocarbene copper(I) complexes, [(DAC)<sub>2</sub>Cu][BF<sub>4</sub>] (**1**), (DAC)CuOSiPh<sub>3</sub> (**2**), (DAC)CuC<sub>6</sub>F<sub>5</sub> (**3**) and (DAC)Cu(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) (**4**) (DAC = 1,3-bis(2,4,6-trimethylphenyl)-5,5-dimethyl-4,6-diketopyrimidinyl-2-ylidene) have been investigated. Complex **1** shows a high photoluminescence quantum efficiency ( $\Phi_{\text{PL}}$ ) in both the solid state ( $\Phi_{\text{PL}} = 0.85$ ) and in CH<sub>2</sub>Cl<sub>2</sub> solution ( $\Phi_{\text{PL}} = 0.65$ ). The emission band of **1**, both as a crystalline solid and in solution, is narrow (fwhm = 2300 cm<sup>-1</sup>) relative to the emission bands of **2** (fwhm = 2900 cm<sup>-1</sup>) and **3** (fwhm = 3700 cm<sup>-1</sup>). Complexes **2** and **3** are each brightly luminescent in the solid state ( $\Phi_{\text{PL}} = 0.62$  and 0.18, respectively), but markedly less so in CH<sub>2</sub>Cl<sub>2</sub> solution ( $\Phi_{\text{PL}} = 0.03$  and < 0.01, respectively). Complex **4** is not emissive in either the solid state or in solution. Phosphorescence of **1** in CH<sub>2</sub>Cl<sub>2</sub> solution shows negligible quenching by oxygen in CH<sub>2</sub>Cl<sub>2</sub> solution. This insensitivity to quenching is attributed to the excited state redox potential being insufficient for electron transfer to oxygen.

## Introduction

Phosphorescent Cu(I) complexes have received a great deal of attention for their use in applications including organic light emitting diodes (OLEDs),<sup>1-4</sup> solar-energy conversion,<sup>5, 6</sup> sensors,<sup>7-9</sup> and biological systems.<sup>10, 11</sup> In the case of OLEDs, Cu(I) complexes have been considered as potential alternatives to the successful phosphorescent emitters using noble-metals<sup>12-14</sup> due to the low cost of copper relative to such elements as iridium and platinum.<sup>1, 15, 16</sup> The most extensively studied mononuclear luminescent Cu(I) complexes are four-coordinate tetrahedral homo- and heteroleptic complexes bearing diimine and organophosphine ligands.<sup>17-22</sup> Recently, a variety of three-coordinate luminescent Cu(I) complexes bearing N-heterocyclic carbene (NHC) ligands have also been reported.<sup>23-27</sup> Interestingly, while the catalytic properties of two-coordinate (NHC)Cu(I) complexes have been investigated extensively,<sup>28-35</sup> reports of their luminescent properties have only appeared recently.<sup>36, 37</sup> This oversight may be due to a previous belief that three and four-coordinate geometries at the copper center are required for efficient luminescence.<sup>21, 23, 38-43</sup>

In this work, we have investigated four linear diamidocarbene Cu(I) complexes (Figure 1), the previously reported [(DAC)<sub>2</sub>Cu][BF<sub>4</sub>] (**1**)<sup>30</sup> and (DAC)Cu(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) (**4**),<sup>44</sup> and two new compounds, (DAC)CuOSiPh<sub>3</sub> (**2**) and (DAC)CuC<sub>6</sub>F<sub>5</sub> (**3**) (DAC = 1,3-bis(2,4,6-trimethylphenyl)-5,5-dimethyl-4,6-diketopyrimidinyl-2-ylidene). Diamidocarbenes display a combination of reduced  $\sigma$ -donor and greater  $\pi$ -acceptor properties relative to their diamino counterparts.<sup>45-48</sup> We show that the bis(diamidocarbene) complex **1** exhibits high photoluminescence quantum efficiency in CH<sub>2</sub>Cl<sub>2</sub> solution and its phosphorescence is

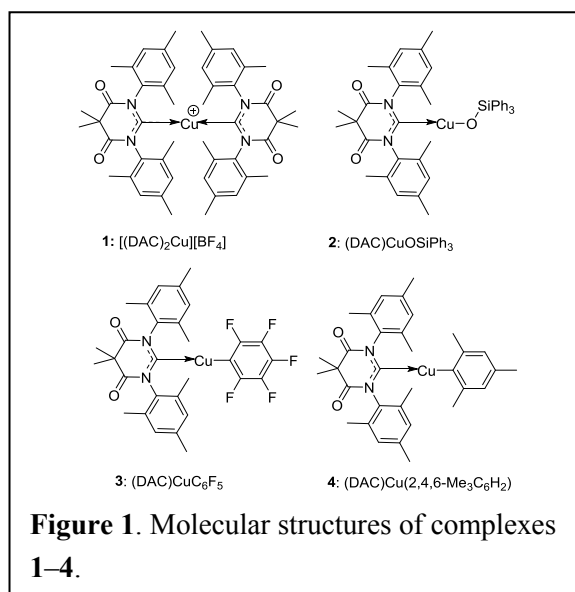
only weakly quenched under aerobic conditions, which differs from most other luminescent Cu(I) complexes.<sup>7-9</sup> (Figure 1).

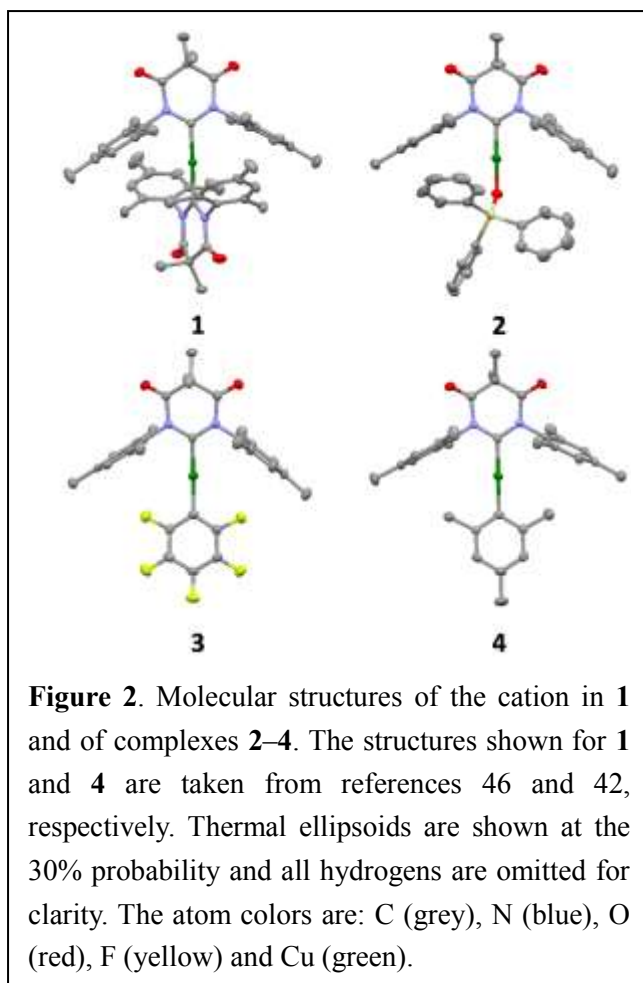
## Results and Discussion

### Synthesis and X-ray structures

Complexes **1** and **4** were synthesized according to literature procedures.<sup>30, 44</sup> Complexes **2** and **3** were formed by protonolysis of either (DAC)CuO<sup>t</sup>Bu or **4** with Ph<sub>3</sub>SiOH or C<sub>6</sub>F<sub>5</sub>H and isolated in 86% and 53% yield, respectively. Whereas the formation of **2** took place rapidly (<1 h) at room temperature, protonolysis with pentafluorobenzene required heating to 333 K for ca. 12 h, reflecting the higher acidity of the silanol (Ph<sub>3</sub>SiOH, pK<sub>a</sub> = 10.8;<sup>49</sup> C<sub>6</sub>F<sub>5</sub>H, pK<sub>a</sub> = 24.2).<sup>50</sup> Complex **1** is indefinitely stable to air, whereas **2–4** are each air- and moisture-sensitive in solution and the solid state.

Single crystals of the compounds suitable for X-ray diffraction studies were grown from CH<sub>2</sub>Cl<sub>2</sub>/hexane (**1**), toluene/hexane (**2**) or by slow evaporation of arene/hexane solutions (**3** and **4**) to afford the molecular structures shown in Figure 2. The crystal structure of [(DAC)<sub>2</sub>Cu]<sup>+</sup> is for [(DAC)<sub>2</sub>Cu][PF<sub>6</sub>].<sup>48</sup> The photophysical studies discussed below were carried out with [(DAC)<sub>2</sub>Cu][BF<sub>4</sub>], but we do not expect the structure of the (DAC)<sub>2</sub>Cu<sup>+</sup> ion to be dependent on the identity of the counter ion. Compounds **1–4** all have monomeric, two-coordinate





structures with a linear geometry around the copper center (**1**:  $178.4(1)^\circ$ ;<sup>48</sup> **2**:  $178.8(1)^\circ$ ; **3**:  $175.4(1)^\circ$ ; **4**:  $179.7(1)^\circ$ ).<sup>44</sup> The Cu–C<sub>NHC</sub> bond lengths in **1** ( $1.926(2)$  Å and  $1.927(2)$  Å)<sup>48</sup>, **2** ( $1.858(2)$  Å), **3** ( $1.902(3)$  Å), and **4** ( $1.905(3)$  Å)<sup>44</sup> are comparable to the values reported for diaminocarbene Cu(I) complexes.<sup>23, 24, 35, 51, 52</sup> The significantly longer Cu–C<sub>NHC</sub> distances in **1**, **3** and **4** compared to that of **2** and (DAC)CuCl ( $1.886(2)$  Å)<sup>48</sup> are consistent with added

steric repulsion arising from the presence of a second carbene ligand or a 2,6-disubstituted aryl group.

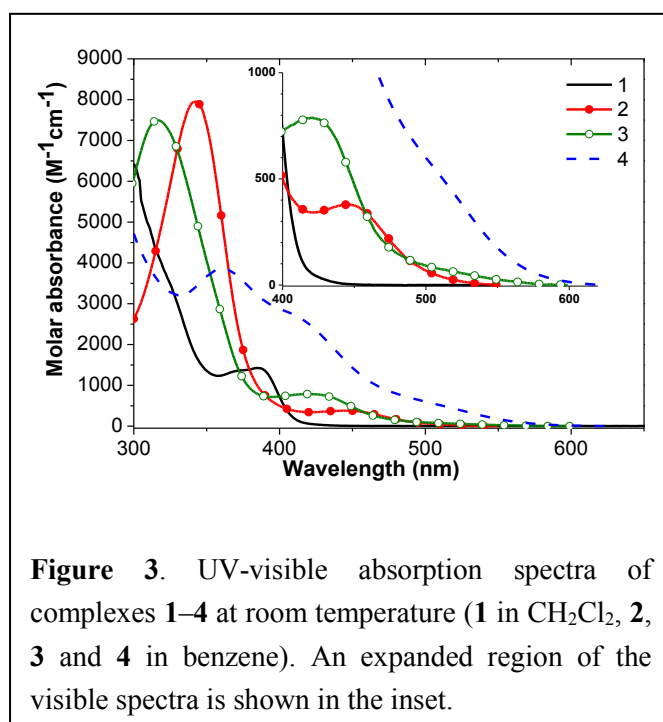
The torsion angle between the planes of the two carbene ligands in complex **1** (defined as the angle between the N–C–N planes of the DAC ligands =  $71^\circ$ ) is close to values found in other [(NHC)<sub>2</sub>Cu]<sup>+</sup> complexes bearing bulky N-aryl-substituted carbenes.<sup>30, 35, 51, 53</sup> For complex **2**, the Cu–O–Si angle ( $133.5(1)^\circ$ ) and the torsion angle between the carbene ligand and Cu–O–Si plane ( $76^\circ$ ) are both similar to those found for (IPr)CuOSiMe<sub>2</sub>Ph (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).<sup>52</sup> In contrast to the approximately perpendicular ligand planes in **1** and **2**, the copper bound aryl groups in complexes **3** and **4** are

nearly coplanar with the diamidocarbenes, having respective dihedral angles of 12° and 7°.

The Cu–C<sub>6</sub>F<sub>5</sub> distance (1.922(3) Å) in complex **3** is significantly longer than that in (py)CuC<sub>6</sub>F<sub>5</sub> (Cu–C<sub>6</sub>F<sub>5</sub> = 1.891(2) Å),<sup>54</sup> but shorter than in three-coordinate (IPr)Cu(tfppy) (Cu–C<sub>6</sub>F<sub>5</sub> = 1.969(5) Å, tfppy = 2-(2,3,4,5-tetrafluorophenyl)pyridine).<sup>38</sup> The Cu–C(mesityl) distance of 1.927(3) Å in complex **4** is comparable to the values found in (iPr<sub>2</sub>Me<sub>2</sub>)Cu(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) (1.922(4) Å, iPr<sub>2</sub>Me<sub>2</sub> = 1,3-di-isopropyl-4,5-dimethylimidazol-2-ylidene)<sup>55</sup> and (IPr)Cu(2-MeOC<sub>6</sub>H<sub>4</sub>) (1.9155(18) Å).<sup>56</sup>

### Photophysical properties

Absorption spectra for complexes **1–4** in CH<sub>2</sub>Cl<sub>2</sub> are shown in Figure 3, data is given in Table 1. Strong bands in the UV region ( $\lambda < 300$  nm) are assigned to  $\pi$ - $\pi^*$  transitions on the ligands. Absorption bands at lower energy are assigned to charge transfer (CT) transitions as



they are absent in the free ligands.

Relatively intense bands between 300–400 nm in **1** ( $\epsilon = 1.4 \times 10^3$  M<sup>-1</sup>cm<sup>-1</sup>) and **2** and **3** ( $\epsilon > 7 \times 10^3$  M<sup>-1</sup>cm<sup>-1</sup>), including those between 350–450 nm in **4**, are tentatively assigned to singlet metal-to-ligand charge transfer (<sup>1</sup>MLCT) transitions. Bands with lower intensity ( $\epsilon < 1 \times 10^3$  M<sup>-1</sup>cm<sup>-1</sup>) at lower energy are

<b>Table 1.</b> Absorption data for complexes <b>1–4</b> .	
	$\lambda_{\text{max}}(\text{nm})$ ( $\epsilon$ , $10^3 \text{ M}^{-1} \text{ cm}^{-1}$ )
<b>1</b>	325sh (3.58), 375 (1.37), 385 (1.42)
<b>2</b>	343 (7.96), 447 (0.38)
<b>3</b>	317 (7.50), 420 (0.79)
<b>4</b>	361 (3.86), 410sh (2.73), 510sh (0.52)
<sup>a</sup> Absorption spectra recorded in $\text{CH}_2\text{Cl}_2$ .	

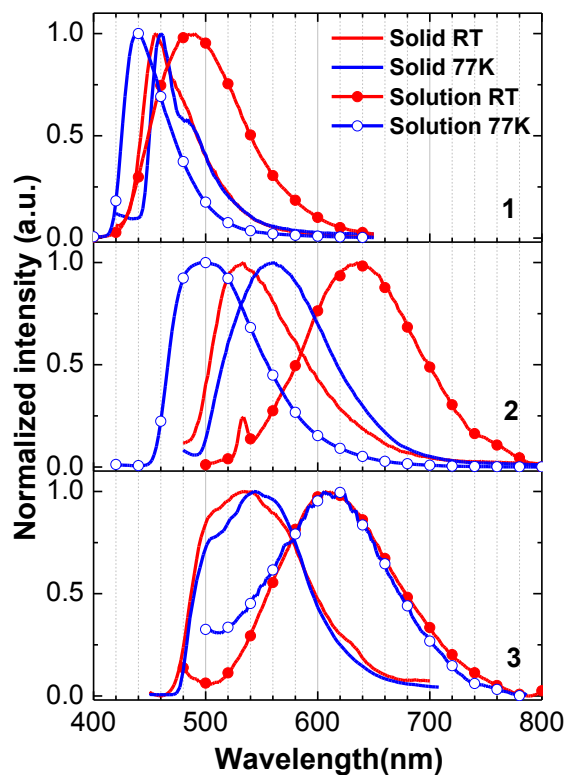
assigned to CT states with ligand-to-ligand character. Weak shoulders ( $\epsilon < 2 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$ ) at the lowest energies of these CT bands likely correspond to triplet CT states admixed with

states having significant singlet character (Figure 3, inset). The bands at energies between 400–550 nm for complexes **2–4** can be assigned to charge transfer (CT) transitions involving the non-carbene ligands since no equivalent low energy absorption features are present in the bis-carbene complex **1**.

Emission spectra for complexes **1–3** in the solid state and in solution are shown in Figure 4, and the photophysical data are summarized in Table 2. In the solid state, complex **1** gives bright blue emission, **2** and **3** display yellow-green emission and **4** is non-emissive. The full width half maximum (fwhm) value for the emission band of solid **1** is narrower (fwhm =  $2300 \text{ cm}^{-1}$ ) than that of **2** (fwhm =  $2900 \text{ cm}^{-1}$ ) and **3** (fwhm =  $3700 \text{ cm}^{-1}$ ). The long lifetimes ( $\tau > 10 \text{ } \mu\text{s}$ ) found for the three compounds as either neat solids or in frozen solution can be fit to single exponential decays and are indicative of emission (phosphorescence) from triplet excited states. The broad emission bands of **2** and **3** are consistent with luminescence from a triplet charge transfer ( $^3\text{CT}$ ) state, whereas the narrower profile in **1** is indicative of a greater degree of intraligand ( $^3\text{IL}$ ) character in the excited state. There is a less than two-fold increase in emission lifetimes upon cooling the solid samples to 77 K, suggesting that thermally activated delayed fluorescence (TADF) does not contribute significantly to the luminescent

properties of these complexes.<sup>25</sup>

The photoluminescent quantum efficiency ( $\Phi_{\text{PL}}$ ) of complexes **1–3** are quite high in the solid state, reaching 0.85 for **1** and 0.18 for **3**. The variation in  $\Phi_{\text{PL}}$  follows the trend in radiative rate constants ( $k_{\text{r}}$ ), which decrease in the order **1** > **2** > **3**, whereas the nonradiative rate constants ( $k_{\text{nr}}$ ) increase in the order **1** < **2** < **3**. The trend in  $k_{\text{r}}$  indicates that **1** has the greatest amount of perturbing singlet character in its triplet state, whereas **3** has the lowest amount. The increase in  $k_{\text{nr}}$  from **1** to **2** can be a consequence of following Energy Gap Law



**Figure 4.** Emission spectra of complexes **1–3** in the solid state and in solution (**1** in  $\text{CH}_2\text{Cl}_2$  at RT and ethanol at 77 K, **2** and **3** in  $\text{CH}_2\text{Cl}_2$  at RT and 2-MeTHF at 77 K).

behavior;<sup>57, 58</sup> however, the larger increase in **3** appears to be caused to additional nonradiative decay processes in the compound. The emission profiles for **1** and **3** in the solid state do not change markedly upon cooling to 77 K, whereas the spectrum for **2** broadens and undergoes a 28 nm red-shift. In contrast, the emission spectra for all three compounds broaden and undergo large bathochromic shifts ( $\Delta\lambda_{\text{max}}$ ) in  $\text{CH}_2\text{Cl}_2$  solution at room temperature ( $\Delta\lambda_{\text{max}} = 34$  nm,  $1500\text{ cm}^{-1}$  for **1**,  $\Delta\lambda_{\text{max}} = 102$  nm,  $3000\text{ cm}^{-1}$  for **2** and  $\Delta\lambda_{\text{max}} = 72$  nm,  $2200\text{ cm}^{-1}$  for **3**). The emission spectra are weakly solvatochromic: compound **1** displays a 10 nm hypsochromic shift



in polar CH<sub>3</sub>CN, whereas **2** and **3** undergo bathochromic shifts of 16 nm and 22 nm, respectively, in non-polar benzene (Figures S17–19, ESI). The hypsochromic shifts in solvents with high polarity (CH<sub>3</sub>CN for **1**, CH<sub>2</sub>Cl<sub>2</sub> for **2** and **3**) indicate that the excited state is destabilized, and thus less polar, than the ground state.

Solution studies at low temperature were performed in ethanol for **1** as the compound was insoluble in 2-methyltetrahydrofuran (2-MeTHF), whereas **2** and **3**, while non-emissive in 2-MeTHF at room temperature, are strongly emissive in the same solvent at 77 K. The emission spectra in solution for both **1** and **2** display large hypsochromic shifts (50 nm for **1** and 140 nm for **2**) upon cooling to 77 K, whereas the spectrum for **3** is relatively unchanged. The rigidochromic shifts in **1** and **2** indicate that both compounds undergo large conformation changes in frozen media. In contrast, the structure of compound **3** is effectively unchanged in both fluid and rigid solvent. A structural change that can account for these differing behaviors is rotation of the ligand around the Cu–ligand bond axis. Examination of the X-ray crystal structures (Figure 2) shows the aryl rings of adjacent ligands in **1** and **2** can have close contact if both ligands are allowed to freely rotate. Therefore, significant structural changes caused by steric conflicts between opposing ligands can be expected when either complex is dissolved in fluid media. However, the C<sub>6</sub>F<sub>5</sub> group in **3** presents a small degree of steric hindrance with respect to the adjacent DAC ligand, and thus only minor distortion is likely to occur amongst the various rotational conformers in the complex.

The luminescent efficiency for both complexes **2** and **3** are also much lower in solution (**2**;  $\Phi_{\text{PL}} = 0.03$ , **3**;  $\Phi_{\text{PL}} < 0.01$ ) compared to **1**, which surprisingly remains highly emissive ( $\Phi_{\text{PL}} =$

Table 1. Luminescent properties of complexes <b>1–3</b> in the solid state and solution. <sup>a</sup>												
Solid at room temperature						Solid at 77 K		Solution at room temperature <sup>b</sup>			Solution at 77 K <sup>c</sup>	
	$\lambda_{\text{max}}$ (nm)	$\tau$ ( $\mu\text{s}$ ) <sup>d</sup>	$\Phi_{\text{PL}}$ <sup>e</sup>	$k_{\text{r}}$ ( $10^4$ $\text{s}^{-1}$ )	$k_{\text{nr}}$ ( $10^4$ $\text{s}^{-1}$ )	$\lambda_{\text{max}}$ (nm)	$\tau$ ( $\mu\text{s}$ ) <sup>d</sup>	$\lambda_{\text{max}}$ (nm)	$\tau$ ( $\mu\text{s}$ ) <sup>d</sup>	$\Phi_{\text{PL}}$ <sup>e</sup>	$\lambda_{\text{max}}$ (nm)	$\tau$ ( $\mu\text{s}$ ) <sup>d</sup>
<b>1</b>	456	18	0.85	4.7	0.83	460	19	490	18	0.65	440	20
<b>2</b>	534	16	0.62	3.9	2.4	562	20	636	1.2	0.03	496	16
<b>3</b>	534	12	0.18	1.5	6.8	543	13	606	0.37	<0.01	606	17

<sup>a</sup> Complex **4** is non-emissive in either solid state or solution. <sup>b</sup> Recorded in CH<sub>2</sub>Cl<sub>2</sub>.  
<sup>c</sup> Complex **1** recorded in ethanol, **2** and **3** in 2-MeTHF. <sup>d</sup> Error in  $\tau$  is  $\pm 5\%$ . <sup>e</sup> Error in  $\Phi_{\text{PL}}$  is  $\pm 10\%$ .

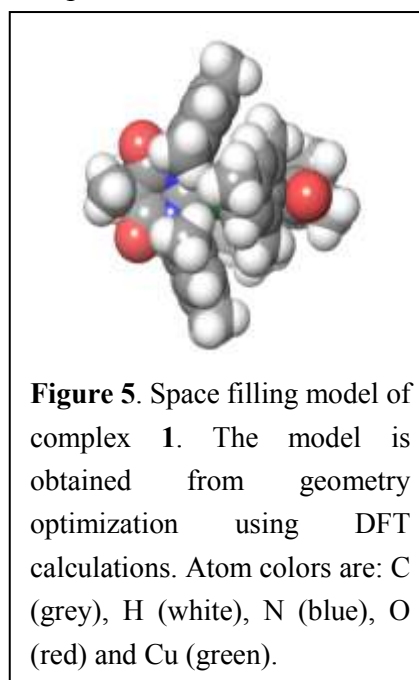
0.65). Copper(I) complexes generally have a significantly higher quantum efficiency as crystalline solids than in fluid solution.<sup>21, 40, 42, 59</sup> The geometry of the compound is held rigidly in place in a crystalline sample, whereas structural relaxation in the excited state can occur more easily in fluid solution leading to both red shifted emission and enhanced non-radiative decay. Mononuclear Cu complexes having  $\Phi_{\text{PL}} > 0.40$  in fluid solution are rare with only a few examples being previously reported.<sup>1, 16</sup>

To obtain a better understanding of the outstanding photophysical behavior of complex **1** in fluid solution, a space filling model of the geometry optimized structures for **1** is shown in Figure 5. The steric encumbrance imposed by the 1,3,5- $\text{Me}_3\text{C}_6\text{H}_2$  rings on the N-substituents of the carbene ligands in **1**, in particular the ortho methyl groups, “lock” the aryl rings into positions orthogonal to the N–C–N plane of the diamidocarbene, effectively minimizing excited state deactivation caused by librational motion of the aryl rings. The rigidity of **1** leads

to only a minor decrease in non-radiative decay in fluid solution and a small red-shift in emission.

Further evidence of the significant steric crowding in **1** is provided by the luminescent quenching behaviour in MeCN solution. While the emission efficiency and lifetime are strongly diminished in MeCN ( $\Phi_{\text{PL}} = 0.04$ ,  $\tau = 1.1 \mu\text{s}$ ), the quenching rate constant determined by Stern-Volmer analysis for MeCN in  $\text{CH}_2\text{Cl}_2$  is extremely small ( $k_q = 3.8 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ ) compared to the value found for the *four*-coordinate Cu(I) complex  $[\text{Cu}(\text{dmp})_2]^+$  ( $k_q = 1.8 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ , (dmp = 2,9-dimethyl-1,10-phenanthroline)).<sup>60</sup> The high quenching rate constants of bis(1,10-phenanthroline) Cu(I) complexes in Lewis basic solvents such as MeCN has been proposed to be due to formation of an exciplex involving direct coordination of the solvent to the metal center, which is expected to be precluded in **1**.<sup>42, 59, 61, 62</sup> However, recent work has questioned the strength and nature of this copper-MeCN interaction and has instead attributed the luminescent quenching to the effect of outer-sphere solvation on the  $^3\text{MLCT}$  energy.<sup>63, 64</sup> Regardless, the roughly thousand fold smaller value for the quenching rate constant of **1** by MeCN relative to that of  $[\text{Cu}(\text{dmp})_2]^+$  implies effective steric protection of the copper complex by the DAC ligands.

A commonly cited application for phosphorescent copper complexes is as oxygen sensors, due to the high propensity for oxygen to quench their emission.<sup>7-9</sup> Thus,



a decrease in the luminescent efficiency or lifetime of the complex in a given environment relative to the same complex under anaerobic conditions can be used to quantify the amount of oxygen present. Surprisingly, phosphorescence for **1** is only slightly decreased ( $\Phi_{\text{PL}} = 0.50$ ) when a  $\text{CH}_2\text{Cl}_2$  solution is sparged with  $\text{O}_2$ . Similarly, the luminescent lifetime under nitrogen ( $\tau = 18 \mu\text{s}$ ) is only slightly diminished in oxygenated  $\text{CH}_2\text{Cl}_2$  ( $\tau = 14 \mu\text{s}$ ). This relative insensitivity of the emission intensity and lifetime to oxygen is highly unusual for phosphorescent compounds. There are two possible quenching mechanisms of the triplet excited state by oxygen, involving either electron transfer or energy transfer.<sup>65</sup> For luminescent quenching by electron transfer (eq 1a) to be thermodynamically feasible, the excited state of **1** has to have a sufficient potential for oxidative quenching to be exergonic (eq 1b):



$$\Delta G = -nF[E(\text{O}_2^{0/-1}) - E(\mathbf{1}^{2+/1+*})] \quad 1b$$

Work terms needed to account for coulombic attraction/repulsion between the products and reactants in eq 1b should also be considered, but these values are typically small in solvents with high dielectric constants and for purposes of discussion here will be neglected. The value for  $E(\mathbf{1}^{2+/1+*})$  in eq 1b is usually obtained by subtracting the spectroscopic excited state energy from the oxidation potential i.e.  $[E(\mathbf{1}^{2+/1+*}) = E(\mathbf{1}^{2+/1+}) - E_{0-0}]$ . Unfortunately, we were unable to obtain a value for  $E(\mathbf{1}^{2+/1+})$  as we could not observe a discernible oxidation wave for **1** using cyclic voltammetry in MeCN. However, two distinct reversible reduction waves are present at  $E^{1/2} = -1.48 \text{ V}$  and  $-1.78 \text{ V}$  versus  $\text{Fc}^+/\text{Fc}$  ( $\text{Fc}$  = ferrocene), thus allowing a limiting value for

the thermodynamic potential for quenching by electron transfer to oxygen to be approximated using eqs 2a-b:



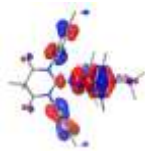
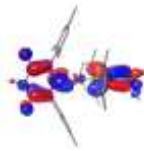

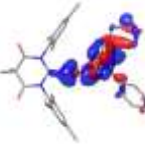


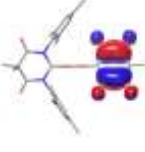
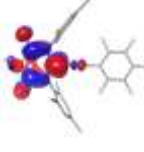

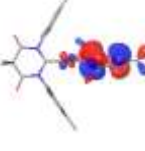
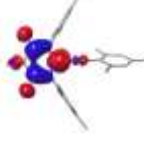

$$\Delta G = -nF[E(\text{O}_2^{0/-1}) - E(\mathbf{1}^{1+/0})] \quad 2b$$

Using the reported value of  $E(\text{O}_2^{0/-1})$  in MeCN (-1.29 V vs  $\text{Fc}^+/\text{Fc}$ )<sup>66</sup> in eq 2b gives an exergonic free energy ( $\Delta G = -0.21$  V). However, a substantial increase in this free energy will be present when quenching  $\mathbf{1}^*$  since a significant coulombic attraction needs to be accounted for in the removal of an electron from  $\mathbf{1}^+$  (eq 1b) as opposed to  $\mathbf{1}^0$  (eq 2b). This change in coulombic interaction can be estimated from the difference between the standard redox couples  $\text{Cu(II)}/\text{Cu(I)}$  and  $\text{Cu(I)}/\text{Cu(0)}$  ( $\Delta E = +0.36$  V).<sup>67</sup> Upon adding this value to eq 2b, electron transfer becomes endergonic and thus, quenching of  $\mathbf{1}^*$  by  $\text{O}_2$  (eq 1a) will be a thermodynamically unfavorable process. This leaves Dexter energy transfer from the triplet state to oxygen (forming singlet oxygen) as a potential quenching pathway. Efficient Dexter energy transfer requires good overlap between the frontier molecular orbitals of both species,<sup>65</sup> which is expected to be severely constrained due to the steric demands of the DAC. Therefore, we can conclude that the relative insensitivity of phosphorescent quenching of  $\mathbf{1}$  by  $\text{O}_2$  is due to the combined effects of the high oxidation potential of the complex along with steric protection of the metal center by the DAC ligands.

## DFT and TD-DFT Calculations

Density functional theory (DFT) calculations were carried out for all of the diamidocarbene complexes using geometric parameters obtained from X-ray analyses as starting structures for **1–4**. The frontier molecular orbital (MO) surfaces calculated for **1–4** are shown in Figure 6. The lowest singlet and triplet vertical energies determined by time-dependent DFT (TD-DFT) calculations are given in Table 3. The optimized ground state structures of **1–4** have a linear coordination geometry at the copper center, with bond lengths that correlate well to the values from the X-ray structures. The torsion angles from the crystal structure and the optimized geometry in complex **1** are similar ( $71^\circ$  and  $79^\circ$  respectively), reflecting the steric constraints of the two DAC ligands. In contrast, the DFT optimized geometry of complex **2** fails to reproduce the large ligand-ligand torsion angle in the crystal structure (X-ray:  $76^\circ$ ; DFT:  $56^\circ$ ). This mismatch between experimental and computational structures is also seen for complexes **3** and **4** and is attributed to steric repulsion between the phenylene and DAC ligands, leading to larger torsion angles in the optimized geometries

**Figure 6.** Frontier orbitals and triplet spin densities calculated for complexes **1–4**.

	HOMO	LUMO	Spin density
<b>1</b>	 -8.85 eV	 -4.97 eV	
<b>2</b>	 -5.90 eV	 -2.60 eV	
<b>3</b>	 -5.85 eV	 -2.66 eV	
<b>4</b>	 -4.86 eV	 -2.49 eV	

when compared to the experimental values measured in the crystal structures (**3**: 12°→24°, **4**: 7°→60°). The optimized structures of the T<sub>1</sub> states in **1**, **3** and **4** retain a linear coordination geometry at the copper center (S<sub>0</sub>→T<sub>1</sub>: **1**: 178°→179°, **3**: 175°→179°, **4**: 180°→178°). Compound **2** has a smaller angle around copper center in the T<sub>1</sub> state (S<sub>0</sub>→T<sub>1</sub>: 179°→156°). The Cu–C<sub>NHC</sub> bond distances decrease ca. 0.05 Å in T<sub>1</sub> state of **1**, **3** and **4** and increase by 0.03 Å in **2**. The bond lengths to the other ligand get either similarly longer (**1** and **3**) or remain unchanged (**2** and **4**). The torsion angles between the ligands in the T<sub>1</sub> state remain unchanged in **1** and **4**, whereas the torsion angles decrease in **3** (78°→56°) and **4** (32°→24°). Interestingly in **4**, despite having a linear C<sub>NHC</sub>–Cu–C<sub>Mes</sub> coordination geometry, the mesityl ring is no longer linearly coordinated to Cu. Instead, the aryl ring is bent with a Cu–C<sub>Mes</sub>–centroid<sub>Mes</sub> angle of 160°.

For complexes **1–4**, the calculated LUMOs have essentially identical orbital character, consisting predominantly of  $\pi^*$  orbitals on the diamidocarbene ligands mixed with *d*-orbitals on copper. However, variation of the non-carbene ligand has a pronounced effect on HOMO composition and orbital energy. For the three heteroleptic Cu(I) complexes, the HOMOs are mainly localized on the metal and the non-carbene ligands. The HOMO energies

**Table 3.** Lowest vertical energy transitions for complexes **1–4** determined from TD-DFT calculations.

Complex	transitions <sup>a</sup>	$\lambda$ (nm)	<i>f</i>
<b>1</b>	S <sub>0</sub> →S <sub>1</sub>	396	0.0058
	S <sub>0</sub> →T <sub>1</sub>	430	0
<b>2</b>	S <sub>0</sub> →S <sub>1</sub>	510	0.0032
	S <sub>0</sub> →T <sub>1</sub>	561	0
<b>3</b>	S <sub>0</sub> →S <sub>1</sub>	494	0.0021
	S <sub>0</sub> →T <sub>1</sub>	540	0
<b>4</b>	S <sub>0</sub> →S <sub>1</sub>	645	0.0049
	S <sub>0</sub> →T <sub>1</sub>	703	0

<sup>a</sup> Orbital contributions to each transition are given in the supplementary information.

of **2** and **3** are similar, but that of **4** is destabilized by 1.0 eV due to the strong electron-donating ability of the mesityl group. TD-DFT calculations of **1–4** show that the calculated wavelength of the  $S_0 \rightarrow S_1$  transitions correlate well with the solution absorption onsets (Table 2). The calculations indicate that the lowest lying triplet transitions for complex **1** is intra-ligand charge transfer (ILCT) admixed with metal-to-ligand charge transfer (MLCT) transitions. The lowest lying triplet transitions for **2–4** are principally MLCT admixed with ligand-to-ligand charge transfer (LLCT) character. The calculated spin density surfaces for the triplet electronic configuration further reflect these same assignments for emissive state showing contours that are principally localized on the DAC ligand and metal center (Figure 6).

## Conclusion

The photophysical properties of a series of four linear, two-coordinate diamidocarbene copper(I) complexes along with a bis-diaminocarbene salt have been investigated. Complex **1** are stable to air and moisture, whereas **2–4** are air- and moisture sensitive. The bis(diamidocarbene) complex **1** displays narrow emission band relative to the other three diamidocarbene species and has a high photoluminescence quantum yield in both the solid state and  $\text{CH}_2\text{Cl}_2$  solution ( $\Phi_{\text{PL}} = 0.85$  and  $0.65$ , respectively). The phosphorescence of **1** is only weakly quenched by  $\text{O}_2$ , which is remarkable for a Cu phosphor with an 18  $\mu\text{sec}$  lifetime. Complex **1** contains a sterically demanding ligand, suggests that the steric bulk of the ligands around Cu is an important factor in designing systems with increased photoluminescence efficiency and suppressed quenching by oxygen. These results echo observations on



mononuclear four-coordinate copper complexes,<sup>16, 21</sup> where increasing the steric bulk of the ligands bound to copper limits the structural changes that occur in the excited state, thereby increasing the luminescence efficiency.

## Experimental

**Synthesis.** All manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques using dried and degassed solvents. Hexane and toluene (purified using an MBraun SPS solvent system) and benzene (refluxed over sodium dispersion) were all dried further over 3 Å molecular sieves and stored over potassium mirrors. THF was refluxed over sodium wire and stored over 3 Å molecular sieves. C<sub>6</sub>D<sub>6</sub> was dried over potassium and vacuum transferred. NMR spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer and referenced to  $\delta$  7.16 (<sup>1</sup>H) and  $\delta$  128.0 (<sup>13</sup>C). <sup>19</sup>F spectra were referenced to CFC<sub>3</sub> at  $\delta$  = 0.0. IR spectra were recorded as KBr discs on a Nicolet Nexus spectrometer. Elemental analyses were performed by the Elemental Analysis Service, London Metropolitan University, London, UK and Elemental Microanalysis Limited, Okehampton, Devon, UK. DAC,<sup>47, 68</sup> [(DAC)<sub>2</sub>Cu][BF<sub>4</sub>] (**1**),<sup>30</sup> (DAC)CuO<sup>t</sup>Bu,<sup>44</sup> [Cu(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)]<sub>n</sub><sup>69</sup> and (DAC)Cu(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) (**4**)<sup>44</sup> were prepared according to literature methods.

**Synthesis of (DAC)CuOSiPh<sub>3</sub> (**2**).** A benzene (20 mL) solution of (DAC)CuO<sup>t</sup>Bu (0.455 g, 0.886 mmol) and Ph<sub>3</sub>SiOH (0.273 g, 0.989 mmol) was stirred at room temperature for 1 h, with a yellow precipitate being generated very early in the reaction. The solvent was removed under reduced pressure, the yellow residue dissolved in a minimum amount of toluene

and reprecipitated by addition of hexane. The solid was cannula filtered, washed with hexane (20 mL) and dried *in vacuo*. Single crystals suitable for X-ray diffraction studies were grown from toluene/hexane. Yield: 0.543 g (86%).  $^1\text{H}$  NMR:  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ , 500 MHz, 298 K) 7.63 (m, 6H, *o*-SiArH), 7.19 (m, 9H, *m*-SiArH and *p*-SiArH), 6.68 (s, 4H, *m*-NArH), 2.05 (s, 6H, *p*-NArCH<sub>3</sub>), 1.93 (s, 12H, *o*-NArCH<sub>3</sub>), 1.30 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta_{\text{C}}$  ( $\text{C}_6\text{D}_6$ , 126 MHz, 298 K) 216.0 (s, NCN), 171.2 (s, CO), 142.7 (s, *i*-SiAr), 139.8 (s, *p*-NAr), 136.0 (s, *i*-NAr), 135.5 (s, *o*-SiAr), 134.1 (s, *o*-NAr), 130.4 (s, *m*-NAr), 128.2 (s, *p*-SiAr), 127.3 (s, *m*-SiAr), 51.3 (s, OC(CH<sub>3</sub>)<sub>2</sub>), 24.3 (s, OC(CH<sub>3</sub>)<sub>3</sub>), 21.1 (s, *p*-NArCH<sub>3</sub>), 18.0 (s, *o*-NArCH<sub>3</sub>). IR ( $\text{cm}^{-1}$ ): 1759 ( $\nu_{\text{CO}}$ ), 1729 ( $\nu_{\text{CO}}$ ). Analysis found: C, 70.45; H, 6.19; N, 4.00.  $\text{C}_{42}\text{H}_{43}\text{N}_2\text{O}_3\text{SiCu}$  requires: C, 70.51; H, 6.06; N, 3.92.

**Synthesis of (DAC)CuC<sub>6</sub>F<sub>5</sub> (3).** C<sub>6</sub>F<sub>5</sub>H (0.150 mL, 1.35 mmol) was added to a benzene (10 mL) solution of (DAC)Cu(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) (0.498 g, 0.89 mmol) in a rigorously flame dried ampoule and the mixture heated at 60 °C for 21 h. After cooling to room temperature, the solvent was removed and the dull orange residue dried *in vacuo*. This was washed with 20 mL of 1:4 v:v benzene/hexane mixture and then with hexane (3 x 10 mL) to give a bright orange powder after drying. Yield: 0.285 g (53%). Single crystals suitable for X-ray diffraction were grown by slow evaporation of a benzene/hexane solution (1:4 v:v).  $^1\text{H}$  NMR:  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ , 500 MHz, 298 K) 6.78 (s, 4H, *m*-NArH), 2.06 (s, 12H, *o*-NArCH<sub>3</sub>), 2.05 (s, 6H, *p*-NArCH<sub>3</sub>), 1.34 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta_{\text{C}}$  ( $\text{C}_6\text{D}_6$ , 126 MHz, 298 K; signals for the C<sub>6</sub>F<sub>5</sub> ligand were not observed) 216.8 (s, NCN), 171.3 (s, CO), 140.4 (s, *p*-NAr), 135.2 (s, *i*-NAr), 134.2 (s, *o*-NAr), 130.4 (s, *m*-NAr), 51.7 (s, C(CH<sub>3</sub>)<sub>2</sub>), 24.3 (s, C(CH<sub>3</sub>)<sub>2</sub>), 21.0 (s, *p*-NArCH<sub>3</sub>), 18.2

(s, *o*-NArCH<sub>3</sub>). <sup>19</sup>F NMR:  $\delta_F$  (C<sub>6</sub>D<sub>6</sub>, 470 MHz, 298 K) -112.5 (m, 2F, *o*-C<sub>6</sub>F<sub>5</sub>), -159.4 (t, <sup>3</sup>*J*<sub>FF</sub> = 20 Hz, 1F, *p*-C<sub>6</sub>F<sub>5</sub>), -163.0 (m, 2F, *m*-C<sub>6</sub>F<sub>5</sub>). IR (cm<sup>-1</sup>): 1763 ( $\nu_{CO}$ ), 1732 ( $\nu_{CO}$ ). Analysis found: C, 59.21; H, 4.72; N, 4.64. C<sub>30</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>F<sub>5</sub>Cu requires: C, 59.35; H, 4.65; N, 4.61.

**X-ray crystallography.** An Agilent Supernova diffractometer equipped with Cu(*K* $\alpha$ ) X-rays was used for data collection on **2**, while a Nonius kappaCCD diffractometer equipped with Mo(*K* $\alpha$ ) X-rays was employed for data acquisition on **4**. Both experiments were conducted at 150 K. Crystal structure solution and refinement was unremarkable in both cases. CCDC 1480899 and 1480900 contain the supplementary crystallographic data for **2** and **4**, respectively. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-1223-336-033; or E-Mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk))

**Density Functional Calculations.** All calculations were performed using Jaguar 9.1 (release 13) software package on the Schrodinger Material Science Suite (v2016-1). Gas phase geometry optimization was calculated using B3LYP functional with the LACVP\*\* basis set as implemented in Jaguar. Geometric parameters obtained from XRD analyses were used as a starting point for geometry optimization in the ground state and triplet state.

**Photophysical Characterization.** The UV-visible spectra were recorded on a Hewlett-Packard 4853 diode array spectrometer. Photoluminescent emission measurements were performed using a Photon Technology International QuantaMaster Model C-60 fluorimeter. Phosphorescent lifetimes were measured by time-correlated single-photon counting using an IBH Fluorocube instrument equipped with an LED excitation source.

Quantum yield measurements were carried out using a Hamamatsu C9920 system equipped with a xenon lamp, calibrated integrating sphere and model C10027 photonic multi-channel analyzer (PMA). All solid and solution samples were prepared in the glovebox prior to performing emission, lifetime, and quantum yield measurements.

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## Notes and References

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† Electronic supplementary information (ESI) available: <sup>1</sup>H spectra in C<sub>6</sub>D<sub>6</sub> (**2**, **3** and **5**) and <sup>19</sup>F NMR spectra of **3** in C<sub>6</sub>D<sub>6</sub>, DFT calculations including lowest vertical energy transitions for complexes **1-5** and atom positions for the optimized ground and triplet excited states. CCDC 1480899 and 1480900. For ESI and crystallographic data in CIF or other electronic format see DOI:

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